# Novel liquid crystal Ester and Its Transition Metal Polychelates

# بلورات سائلة للاستر ومعقداته مع العناصر الاتقالية

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A novel ligand N-(2-hydroxyl phenyl)-(4′-pentloxy-benzate-salicyIidene) ($H_2L$) prepared by 1:1 molar ratio of 4-pentyloxy (4′-formyl-3′-hydroxy)-benzoate and 2-aminophenol, synthesis of $[M(H_2L)H_2O]$ and $[Cu_2L_2]$ complexes were described by IR spectroscopy, C.H.N.O, $^1H$, $^{13}CNMR$, GCmass. TGA/DSC to study Thermal properties, while liquid-crystalline properties was studied by using the (OPM). All the samples show (sematicA).

**الخلاصة :**

تحضير ليكند جديد N-(2-hydroxyl phenyl)-(4-pentloxy-benzate-salicyIidene) من تفاعل 4-pentyloxy (4- formyl-3 –hydroxy-2-aminophenol مع بنسب ١:١ ثم تحضير معقداته مع العاصر الانتقالية والتي كان لها الصيغه تم تشخيص اليكندات ومعقداته بواسط تقنية الاشعه تحت الحمراء بالاضافه الى دراسة الكاربون هايدروجين نايتروجين اوكسجين, ودراسة طيف الرنين لمغناطيسي, كما تم التحليل النوعي للمركبات مع التعرف عليها بواسطة تحديد الايون الجزيئي للعينة بواسطة التأين الإلكتروني بواسطه مطياف الكتلة. اثبتت المواد المحضرة ان لها القابلية ان تكون بلورات سائله واضهرت انماط مختلفه تم مناقشتها تحت المكرسكوب الضوئي

**الكلمات المفتاحية**: قواعد شيف - العناصر انتقالية – بلورات سائلة

## INTRODUCTION

The coordination chemistry of transition ions has been widely investigated in recent years because of both its useful magnetic and optical behaviors. [1] Wide variety of ligands such as Schiff bases ligands have been employed for the synthesis of new classes of transition liquid crystal. [2] The liquid crystal also has enjoyed lot of interests owing to unusual geometries and novel properties such as spin crossover, ferro electricity, photo refractivity, contrast agents for magnetic resonance imagining (MRI), luminescent stains for fluoro immune assays, catalysts for the selective cleavage of RNA and DNA and cancer radio therapeutic agents. [3] Transition temperatures of the Schiff base complexes are greatly influenced by the choice of the counter ion and they were able to show that the metal contraction has a distinct influence on the transition temperatures of this type of

compound. [4] Not only are these ions paramagnetic and have a high magnetic moment but also more importantly, a high value for the magnetic anisotropy is desirable if one wants to switch liquid crystals by an external magnetic field. [5] Many researchers had studied in detail the complexes of Schiff base ligands with one aromatic ring. [6] Schiff base ligands complexes with two aromatic rings have been studied much less intensively, [7] while a new Schiff base ligand contains three aromatic rings and their lanthanide complexes were reported by Binnemans et al. [8] Schiff base ligands with N, O donor sets have often been used since the Schiff base ligands may assemble coordination architectures directed by the lanthanide (III) ions and transition metal.[9] In the study of lanthanide complexes, many different types of ligands are frequently used to link Ln(III). Moreover, the thermodynamic properties of lanthanide complexes are also important for the theoretical study and the practical applications. The doubly deprotonated ligand contains strong donors, namely phenolato oxygen atoms as well as imine nitrogen atoms bearing excellent coordination ability with transition/inner transition metal ions through its NxOy donor set. In our previous work, [6-9] this paper is a continuous work to research A novel mesogenic (smectic), ligand N-(2-hydroxyl phenyl)-(4′-pentloxy-benzate-salicyIidene) ($H_2L$) prepared by 1:1 molar ratio of 4-pentyloxy (4′-formyl-3′-hydroxy)-benzoate and 2-aminophenol, synthesis of [$M(H_2L)H_2O$] and [$Cu_2L_2$] complexes were described by IR spectroscopy, C.H.N.O, $^{1}H$, $^{13}CNMR$, , GCmas, TGA/DSC and POM [10].

**2. Materials and methods**

analytical grade was used for all chemicals. All measurements were carried out at Faculty of Science, UPM University, Malaysia.

**3. Experiment**

***3.1 4-pentyloxybenzoic acid (1)***

Solution of 150 mL ethanol with 11.05 g of hydr0xybenz0ic acid (80 mm0l) and 50 mL ethanol with 8.97 g KOH (160 mm0l), drop wise addition of 10 mL of 1-bromopentane (80 mm0l). refluxed for ~14 h The mixture filtered off The white crude product mixture of glacial acetic acid and toluene were used for crystallization. [10] Yield: (75%) Scheme 1. shows synthesis details.

***3.2 4-pentyloxy (4′-formyl-3′-hydroxy)-benzoate (2)***

Solutions of (50 mmol, 10.40 g in 50 mL) 4-pentyloxybenzoic acid, (50 mmol, 6.90 g in 50 mL) 2,4 dihydroxybenzaldehyde, (55 mmol, 11.35 g in 100 mL) DCC in dry chloroform along with (2.5 mmol, 0.3 g as a catalyst) solid DMAP were magnetically stirred at room temperature for ~12 h. The byproduct (dicyclohexyl urea) was filtered off under suction and the solvent was removed on rotavapor. The crude product was recrystallized from hot solution of ethanol and purified by column chromatography over $SiO_2$ by eluting with a mixture of n-hexane and chloroform (v/v, 1:1); evaporation of this eluent yielded the ester 2, in the form of a white solid [10]. Yield: (62%).flawed

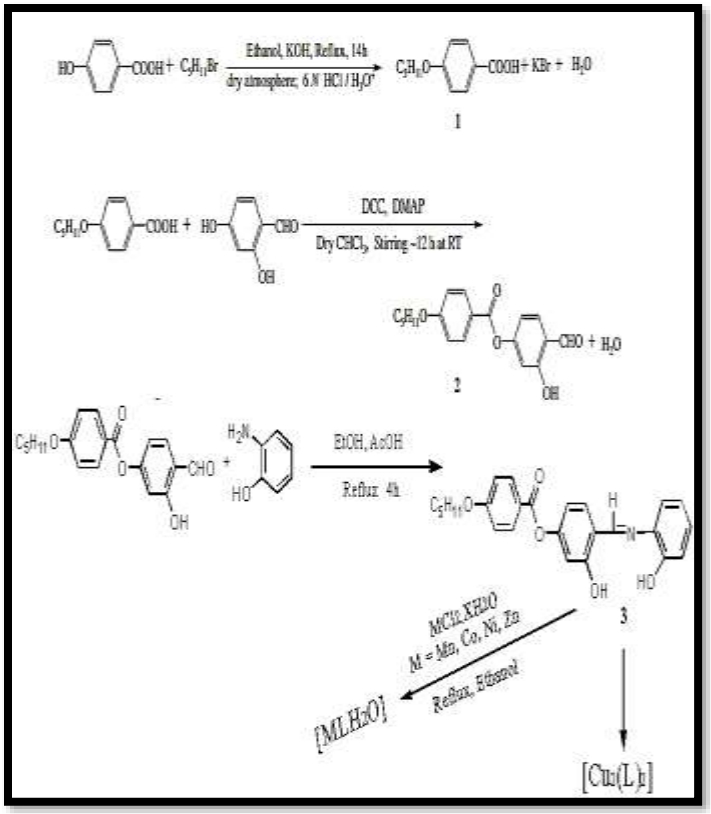
***3.3 Synthesis of N-(2-hydroxyl phenyl)-(4′-pentyloxybenzoate-salicylidene) ($H_2L$) (3)***

Absolute ethanolic solutions of (20 mmol, 6.56 g in 100 mL) 4-pentyloxy-(4′-formyl-3′-hydroxy)benzoate and (20 mmol, 5.64 g in 20 mL) 2-aminophenol were refluxed for ~4 h in presence of a few drops of acetic acid and the resultant solution was left over-night in the reaction flask at room temperature. The micro-crystalline pale yellow product, 3, was suction-filtered,

thoroughly washed with ethanol, recrystallized from a solution of absolute ethanol/chloroform (v/v, 1/1) and dried at room temperature. [10] Yield: (60%); m.p., 89°C.

### *3.4 Synthesis of the Complexes*

All complexes were prepared by adding (1 mmol) of metal salt ($MCl_2.XH_2O$), were M=Mn, Co, Ni, Zn and Cu, dissolved in (25 mL) ethanol to (1 mmol, 0.42 g) of ligand ($H_2L$) in (25 mL) ethanol the resulting solution was stirred and heated on a hot plate at 60 °C for 2 h. The volume of the obtained solution was reduced to one-half by evaporation 1 day later. The precipitated product was filtered, washed with cold ethanol and hot petroleum ether 40–60°C and finally dried under vacuum.




Scheme1: $H_2L$ and its complexes pathway [10].

## RESULTS AND DISCUSSION

M= Co Cu Ni Mn and Zn form mononuclear (1 – 4) complexes with $H_2L$ while complex (5) appear as di-nuclear. All were stable, colored, DMF soluble. All the physical and chemical properties are mention in paper [10].

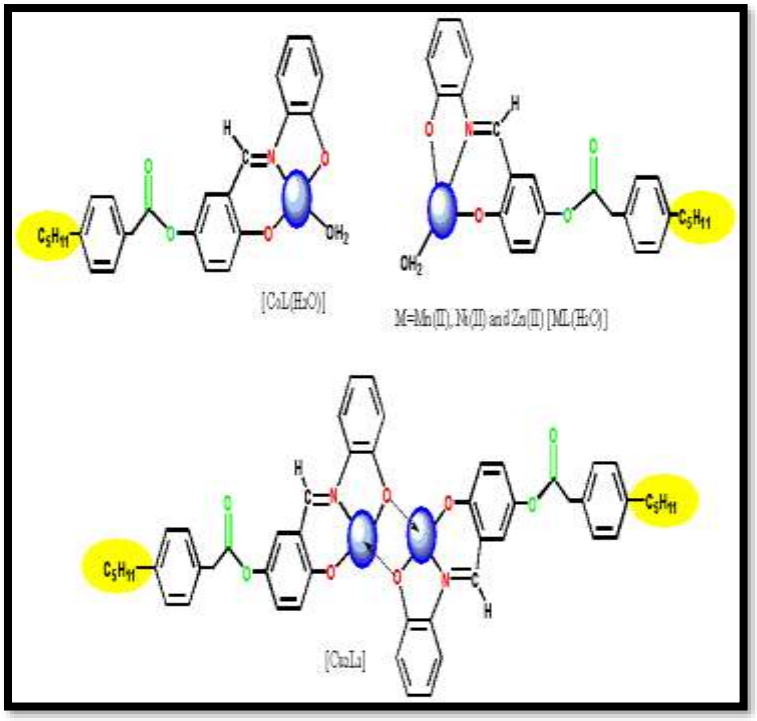


**Fig 1:** $H_2L$ and its complexes [10].

**LIQUID CRYSTAL CHARACTERAZATION**

LCD properties for the ligand and its Polychelates studied by (POM) and (DSC) differential scanning calorimetry [12]. Mono-tropic mesomorphs, was for the ligand $H_2L$, during heating the sample directly change to isotropic liquid and the liquid transformed to batoneets texture in cooling [13], birefringent texture fanlike was merge at 76.3℃ [14]. (Figure 2) solid molecule can be noticed in further cooling at 62℃, all these facts help us to describe the phase as SematicA texture [15]. the ligand second run in DSC shows 1 specific transition and 2 specific transition during heating and cooling cycle respectively (Figure 3) [16]. $\Delta H$ = (3.6 kJ $mol^{-1}$) at 95℃ this change in temperature because of transformation from Isortropi to semantic A texture [17]. The existence of the function -OH group give the privilege to form intermolecular interactions (HO ,,,,,, HO) [18-22] that give the unique liquid crystaline. anti-tropic SmA texture exhibited in all complexes with broken focal conic structure (Figure 4) 125℃ during cooling cycle from isotropic liquid, optical mesophase help to diagnosed it as sematicA . the DSC run shows 2 specific endothermic and 2 specific exothermic during heating and cooling cycle respectively (Figure 5) [23]. Transition at 118–126℃ for Isotropic with SmA , hysteresis change in transition T phenomena appeared in complexes because of the highly viscosity nature which causes difficult restriction in the molecular mobility [24 -26]. DSC confirmed the heating and cooling cycle for all the synthesis complexes in (Table 1) the enantiotropic ligand, N–(2–hydroxyphenyl)–4–n–butylsalicylaldimine liquid crystal with SmA [5] and its Lanthanide (III) complexes with linkage as azo in one side of

aromatic ring have phase Sematic A has been record [10], [26]. observed phases appear like fanlike with pattern clearly seen in the present compounds.

Fig. 2: POM shows Fan texture of ligand and during cooling shows SematicA at 78℃ phase.

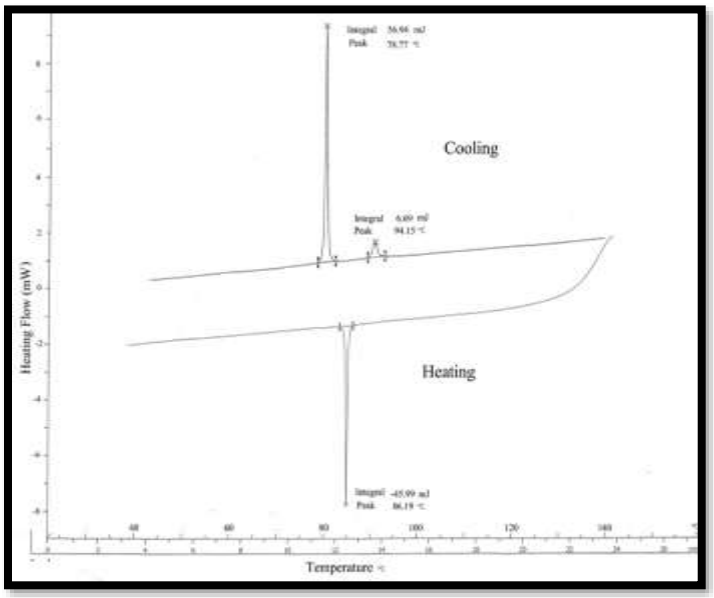



Fig. 3: Second heating in DSC as well as cooling cycle for $H_2L$.

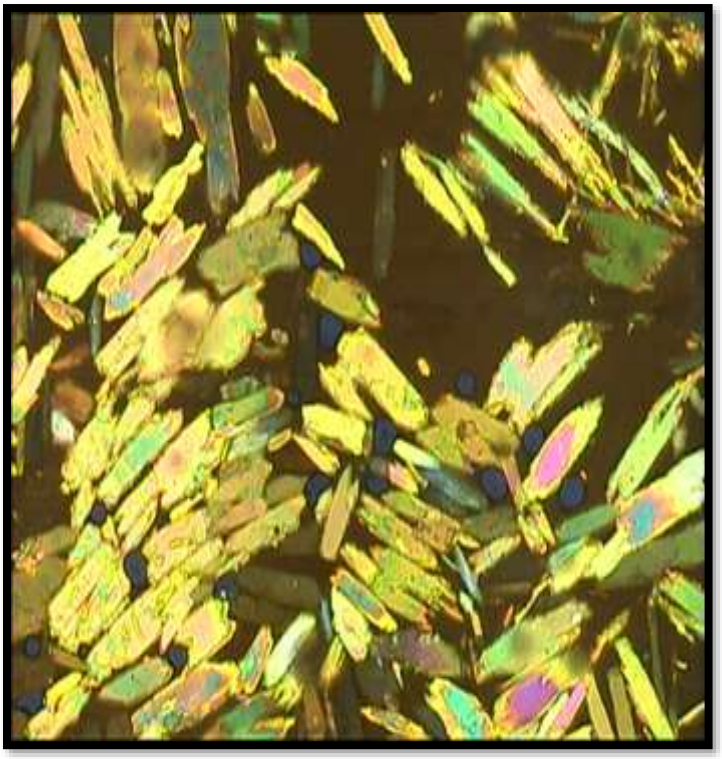


Fig. 4: [$Cu_2L_2$] POM shows Broken focal conic shaped texture , during cooling shows Sematic A at 126°C phase.

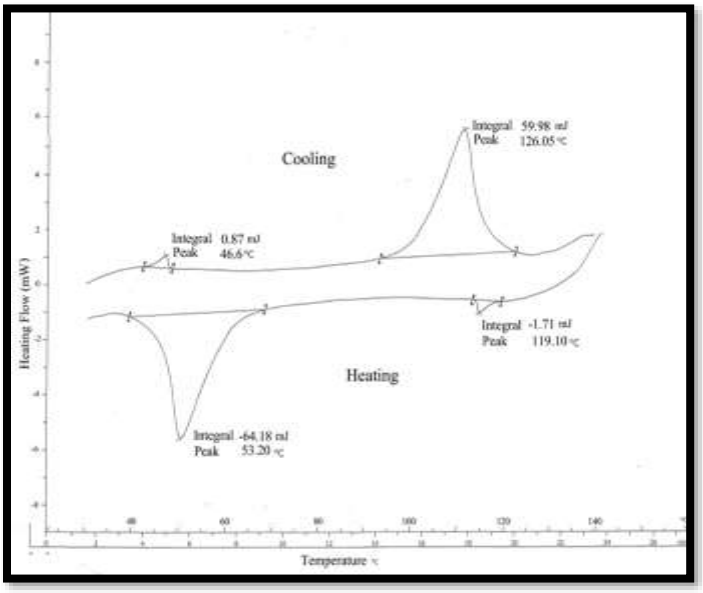



Fig. 5: [$Cu_2L_2$] DSC second heating - cooling cycle.

Table 1: DSC run of $H_2L$ and its Polychelates.

| Compounds | ΔT (T/°C) and related Transition | Δs (kJ.mol-1) values |
|---|---|---|
| ($C_{25}H_{25}NO_5$) | 87 °C (Cr - I) (heating). 95 °C (I – Sm A), 79°C (Sm A - Cr) (cooling). | 76.3 3.6, 28.9 |
| (1) ($MnC_{25}H_{25}NO_5$) | 90 °C (Cr – Sm A), 125 °C (Sm A - I) (heating). 118 °C (I –Sm A), 80 °C (SmA -Cr) (cooling). | 4.2, 25.3 4.5, 38.9 |
| (2) ($CoC_{25}H_{25}NO_5$) | 71 °C (Cr – Sm A), 132 °C (Sm A - I) (heating). 120 °C (I – Sm A), 60 °C (Sm A - Cr) (cooling). | 3.6, 55.9 50.4, 64.7 |
| (3) ($NiC_{25}H_{25}NO_5$) | 68 °C (Cr – Sm A), 144 °C (Sm A - I) (heating). 136 °C (I –Sm A), 71 °C (Sm A - Cr) (cooling). | 2.4, 45.9 58.4, 70.7 |
| (5) ($Cu_2C_{50}H_{46}N_2O_{10}$) | 65 °C (Cr –Sm A), 98 °C (Sm A- I) (heating). 125 °C (I –Sm A), 45 °C (Sm A- Cr) (cooling). | 45.8, 1.2 50.3, 0.73 |

**CONCLUSION**

A novel ligand N-(2-hydroxyl phenyl)-(4′-pentloxy-benzate-salicyIidene) ($H_2L$) prepared by 1:1 molar ratio of 4-pentyloxy (4′-frmyl-3′-hydrxy)-benzoate and 2-aminophen0l, synthesis of [$M(H_2L)H_2O$] and [$Cu_2L_2$] complexes were described by IR, C.H.N.O, $^1H$, $^{13}CNMR$, , GCmass.

square planar suggested for Co(II), Cu(II), complexes, while Mn(II), Zn(II) and Ni(II) shows tetrahedral, thermaly highly stable, the polychelate shows pattern with fanlike texture properties of the enantiotropic SematicA phase with $Cu_2L_2$.

**FUNDING**
We are thankful for University of Putra Malaysia for physical measurements facilities.

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